Strong interplay between structure and magnetism in LaFe$_{11.3}$Co$_{0.6}$Si$_{1.1}$: A neutron diffraction study

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Abstract

Neutron diffraction was employed to investigate the crystallographic and magnetic structures of the cubic NaZn$_{13}$-type intermetallic compound La(Fe$_{11.3}$Co$_{0.6}$Si$_{1.1}$). Rietveld analysis shows that Co atoms preferentially occupy the 96i site. The onset of the ferromagnetic ordering results in a large volume expansion. Even in the ferromagnetic state, the lattice expansion still correlates tightly with the magnetic moments.

1. Introduction

The magnetic refrigerators working near room temperature are strongly wished due to their tight connection with our daily life, for example food cooling, air-condition, etc. Recently, the giant near-room temperature magnetocaloric effect (MCE) induced by first-order magnetic phase transition has attracted extensive attention. Three types of materials have been found: (1) Gd-based alloys Gd$_3$(Si,Ge)$_4$ [1,2]; (2) transition-metal-based phosphide-arsenides MnFe(P,As) [3] and (3) Fe-based rare-earth transition-metal intermetallic compounds La(Fe,Co,Si)$_{13}$ [4] and their hydrides[5]. Derived from the data of the isothermal magnetization measurement, the peak values of the magnetic entropy change $\Delta S_M$ for magnetic field changes from 0 to 5T are 19 J kg$^{-1}$ K$^{-1}$ of Gd$_3$Si$_2$Ge$_2$ at 277 K [1], 18 J kg$^{-1}$ K$^{-1}$ of MnFe(P$_{0.45}$As$_{0.55}$) at 310 K [3], 20.3 J kg$^{-1}$ K$^{-1}$ of La(Fe$_{11.3}$Co$_{0.7}$Si$_{1.1}$) at 274 K [4], respectively. All of these values are nearly twice more than $\Delta S_M$=9.80 J kg$^{-1}$ K$^{-1}$ of Gd (at 293 K) induced by the second-order phase transition.

In the present study, we report the crystallographic and magnetic structures studied by high-resolution neutron powder diffraction in the NaZn$_{13}$-type rare-earth transition-metal intermetallic compound La(Fe$_{11.3}$Co$_{0.6}$Si$_{1.1}$).

2. Experiment

The compound with the nominal composition La(Fe$_{11.3}$. Co$_{0.6}$Si$_{1.1}$) was prepared by arc-melting the element materials with purity of 99.9 wt % under high-purity argon atmosphere, and subsequently annealed at 1273 K for one month in an evacuated quartz tube. Neutron diffraction was carried out on powder sample in the temperature range of 2–350 K on the diffractometer G4.2 [6] installed at the cold neutron guide at the reactor ORPHEE of the Laboratoire Leon Brillouin, France. Incident beam was focusing by Ge monochromator with the wavelength of 2.3433 Å. The data were collected in the range of $2\theta=6–140^\circ$ with a step increment of 0.1°, and analyzed by the program FULLPROF [7].

3. Results and discussion

Powder diffraction patterns confirm that the annealed sample crystallizes in the cubic NaZn$_{13}$-type structure.
(space group: Fm3c) in the whole range of temperature (2–350 K) with ~10% of \( \alpha \)-Fe\textsubscript{11.4}Si\textsubscript{0.6} as a secondary phase. The Co occupancies were determined by refining the diffraction patterns collected at high temperatures \( T > T_C = 259 \) K. Based on the random distribution of Si atoms on both of Fe sites in Co-free iso-structural compound \( \text{La(Fe}_{11.4}\text{Si}_{1.6}) \) [8], Rietveld refinement of data collected at 350 K (Fig. 1(a)) shows that the Co atoms totally locate at the 96i site of Fe atoms (Fe\textsuperscript{II}), not at the 8b (Fe\textsuperscript{I}) site. The refined concentration \( x = 0.59(8) \), is in agreement with the starting nominal composition. It is well known that the positive heat of alloying between La and Fe is considered as the reason why no La–Fe binary compound exists. Since the La atoms are surrounded by the Fe\textsuperscript{II} atoms, one can infer that the preferential substitution of Co atoms in the Fe\textsuperscript{II} sites helps the formation of the cubic NaZn\textsubscript{13}-type structure due to lowering the formation heat effectively.

The magnetic structure was determined by refining the diffraction patterns recorded at low temperatures (\( T < T_C \)) with the fixed Co occupancy at the 96i site. The fact of no additional superlattice reflection implies its ferromagnetic ordering, in agreement with the magnetic measurements. As an example, Fig. 1(b) shows that the collected pattern at 2 K was fitted with ferromagnetic model very well. The magnetic moment values increase from \( \mu(\text{Fe}\textsuperscript{I}) = 2.0(1) \mu_B \), \( \mu(\text{Fe}\textsuperscript{II}) = 2.17(7) \mu_B \) at 250 K up to 2.4(1) \( \mu_B \), 2.90(6) \( \mu_B \) at 2 K, respectively, a bit larger than those in La(Fe\textsubscript{11.4}Si\textsubscript{1.6}) [8] and La(Fe\textsubscript{1-x}Al\textsubscript{x})\textsubscript{13} [9], which seems to imply that the substitution of a small amounts of Co not only significantly enhances the Curie temperature, but also the Fe magnetic moments.

The strong interplay between magnetism and structure is fairly demonstrated by the large lattice expansion induced by the ferromagnetic ordering (Fig. 2). After subtracting the linear thermal expansion with the expansion coefficient \( \alpha \sim 6 \times 10^{-5} \text{K}^{-1} \) as in La(Fe\textsubscript{11.4}Si\textsubscript{1.6}) [8] from the refined lattice constant, we find the expansion of lattice by magnetic ordering reaches ~0.5% when the temperature decreases cross the Curie temperature. Even below \( T_C \), the pure spontaneous volume magnetostriiction \( \omega_s \), in terms of \( \Delta V/V = 3\Delta l/l \), still interplays with the magnetization (Fig. 2 inset). Theoretically, in strongly, or immediately, correlated ferromagnetic system, the spontaneous volume magnetostriction \( \omega_s \) can be written as \( \omega_s = kCM^2(T) \), where \( kC \) is magnetic volume coupling constant and \( M(T) \) magnetization. As seen in inset of Fig. 2, the spontaneous volume magnetostriction \( \omega_s \) is obviously consistent with the above item, giving \( kC = 5.66 \times 10^{-5} \text{cm}^3/\text{emu}^2 \), a half of that in the iso-structural compound La(Fe\textsubscript{11.4}Si\textsubscript{1.6}), which seems to imply that Co-substitution lowers the magnetic–lattice coupling. Note that \( \omega_s \sim 1.8\% \) at 2 K is the same as in La(Fe\textsubscript{11.4}Si\textsubscript{1.6}) [8].

In summary, neutron powder diffraction was employed to investigate the crystallographic and magnetic structures of the NaZn\textsubscript{13}-type intermetallic compound LaFe\textsubscript{11.3}Co\textsubscript{0.6}Si\textsubscript{1.1}. The preferential substitution of Co atoms at Fe\textsuperscript{II} 96i site effectively lowers the La–Fe positive heat of formation to stabilize the cubic NaZn\textsubscript{13}-type structure. The lattice expands sharply with the long-range ferromagnetic ordering, and still tightly interplays with the local Fe moments to low temperature, resulting in the magnetovolume coupling constant \( kC = 5.66 \times 10^{-5} \text{cm}^3/\text{emu}^2 \) and the spontaneous volume magnetostriction \( \omega_s = 1.8\% \) at 2 K.

![Fig. 1. Neutron diffraction patterns of La(Fe\textsubscript{11.4}Co\textsubscript{0.6}Si\textsubscript{1.1}) at (a) \( T = 350 \) K, and (b) \( T = 2 \) K. The full lines represent the refined fits as described in the text. The markers represent the calculated peak positions. The difference between observed and calculated data are given at the bottom.](image1)

![Fig. 2. Lattice parameter and average magnetic moments per Fe atom from the final refinement as a function of temperature. Inset: the spontaneous volume magnetostriction \( \omega_s \) as a function of squared magnetization \( M^2 \) of La(Fe\textsubscript{11.4}Co\textsubscript{0.6}Si\textsubscript{1.1}).](image2)
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